Ionic Velocities in Air at Different Temperatures.

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The object of this paper is to find at different temperatures the velocity in an electric field of the ions produced by Röntgen rays in air at atmospheric pressure. The different values obtained will tell us whether the masses of the ions depend in any way upon the temperature.

Langevin,* in 1902, described a new method which he had devised to determine the velocities of ions in an electric field. The principle of the method is as follows:—

A and B are two parallel plates distant d apart. A can be earthed or connected to one pair of quadrants of an electrometer and B can be raised to a given potential, and at any instant that potential can be reversed.

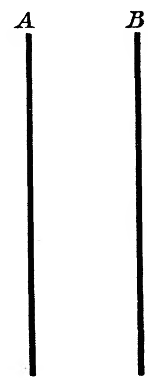


Fig. 1.

With B at a given positive potential, a single discharge is sent through a Röntgen bulb which ionises the air between A and B. Let us suppose that the ionisation is uniform. At a certain time t after the discharge has passed in the bulb, the potential on B is reversed.

If we represent by a curve the quantity received by A when t is altered we shall get a curve of the form given in fig. 2. By varying the time t and measuring the quantity received by A

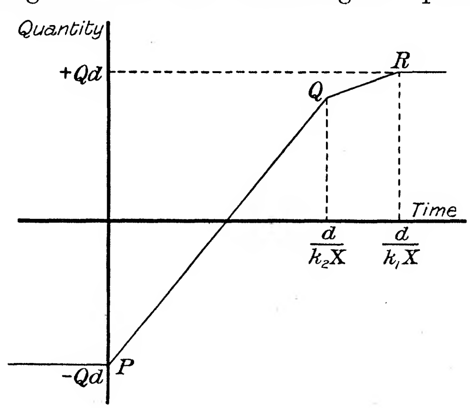


Fig. 2.

* Langevin, 'Recherches sur les gaz ionisés,' Paris, 1902.

we can experimentally realise this curve and so obtain the points of discontinuous curvature, P, Q, and R. The time between P and Q is d/k_2X and between P and R is d/k_1X, where k_1 and k_2 are the velocities under unit field of the positive and negative ions respectively, and X is the field. Knowing t, X, and d, we calculate k_1 and k_2.

If the ionisation be not uniform but be localised close to one of the plates, the form of the curve will be altered.

Suppose the ionisation is very intense close to A and that before reversal B is positive, then the form of the curve will be that given in fig. 3, while, if B is negative before the reversal, the form will be that given in fig. 4.

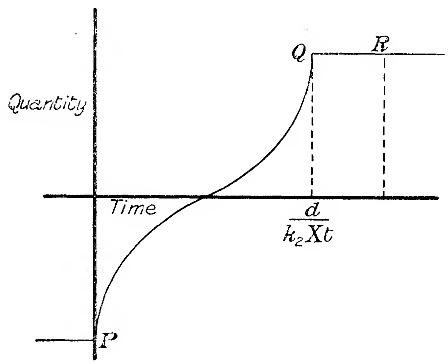


Fig. 3.

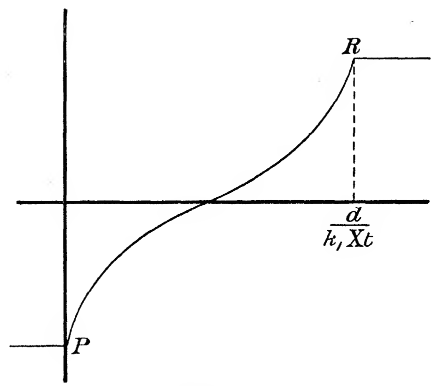


Fig. 4.

We see that in the first case the point Q of discontinuous curvature is very marked and in the second case R is very clearly marked. Using localised ionisation in this way we can find the points with greater precision.

In this investigation we have neglected the effect caused by diffusion and recombination of the ions and by the distortion of the field due to unequal distribution of the ions.

Langevin, in the thesis already referred to, has shown that diffusion and recombination only round off the corners on the curve and do not displace them; consequently the experimental curve will inform us whether these are serious. Langevin also shows that the distortion of the field is negligible if the total charge received by the plate A is less than a quarter of the charge induced on A when the potential on B is raised from zero to the potential used in the experiment. In my experiments this fraction never rose above one-twentieth.

The general arrangement of the apparatus, by means of which this method was experimentally realised, is shown in fig. 5, and is essentially the same as that described by M. Langevin.

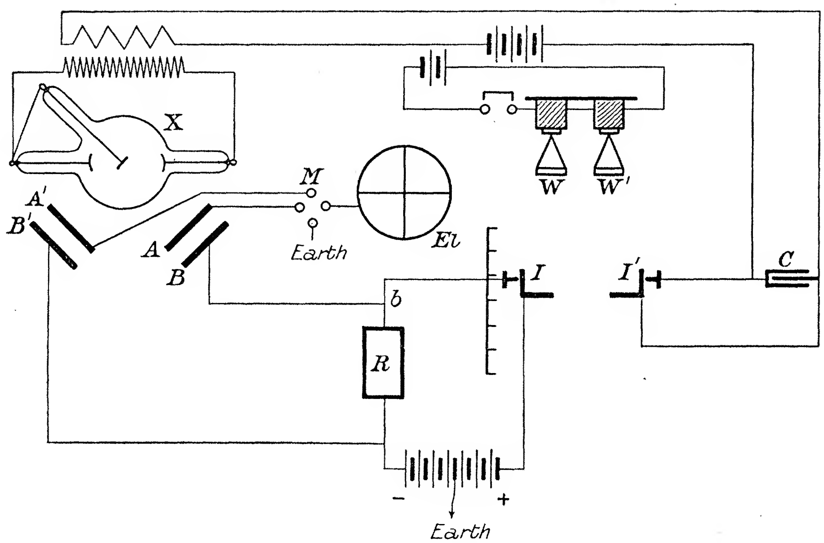


Fig. 5.

W and W′ are two weights which can be allowed to fall simultaneously and break the contacts I and I′. The breaking of the contact at I′ causes a single discharge to pass through the Röntgen bulb X, while the breaking at I reverses the potential on the electrode B.

I can be fixed at any point on a vertical scale, and thus the contact may be broken at any required time before or after it is broken in I′. As in M. Langevin's experiments, a standard pair of electrodes, A′B′, is used, and the ratio of the charge received by A to that received by A′ is the quantity which is plotted against the time in order to obtain the experimental curves.

For a fuller account of the apparatus, *vide* Langevin's thesis.

When the ionisation used is intense close to one of the plates, as in figs. 3 and 4, a null method may be used. A′B′ are so adjusted that when we travel along the horizontal parts of the curve, A′ receives an equal and opposite charge to A. A and A′ are connected together and to the electrometer, and so, while we remain on the horizontal part of the curve, we shall get no deflection, but as soon as we get beyond P, Q, or R, as the case may be, we shall get a deflection.

This is a very convenient and quick method of obtaining the position of the points, and it is used in most of the experiments described in this paper.

The electrometer has a fine phosphor-bronze suspension, gives 496 mm. deflection for 1 volt between the two pairs of quadrants, and has a capacity of about 61·5 cm.

It was found convenient to use different forms of vessel at different

temperatures, and so the description of the vessel in which A and B are enclosed will be reserved for the account of the experiments at the various temperatures.

The experiment has been carried out at the following temperatures absolute:—94°, 209°, 285°, 333°, 348°, 373°, 383°, 399°, and 411°, *i.e.*, at temperatures ranging from −179° C. to +138° C.

Between −64° C. and +138° C. the velocities of both the positive and negative ions are very nearly directly proportional to the absolute temperature, but at −179° C. the two velocities seem to be equal and much smaller than would be given by this linear law.

Determination of the Velocities at the Temperature of Boiling Liquid Air.—In order to reduce the size of the ionisation vessel as much as possible the plane parallel electrodes were replaced by concentric cylindrical ones. This slightly alters the calculation. Let the diameter of the outer cylinder be b, of the inner a.

Then at a point between a and b distant r from the centre the electric intensity is equal to $\frac{1}{r} \cdot \frac{V}{\log b/a}$, where V is the difference of potential between a and b. The velocity of the positive ions at this point will be

$$\frac{dr}{dt} = k_1 \frac{1}{r} \cdot \frac{V}{\log b/a};$$

therefore

$$\int_a^b r\,dr = \frac{k_1 V}{\log b/a} \int_0^{T_1} dt,$$

where T_1 is the time which a positive ion would take to travel from a to b, *i.e.*, the time between the two discontinuities P and R.

Thus

$$\frac{b^2-a^2}{2} = k_1 \frac{V}{\log b/a} \cdot T_1,$$

i.e.,

$$k_1 = \tfrac{1}{2}(b^2-a^2)\log\frac{b}{a} \cdot \frac{1}{VT_1}.$$

Similarly, for the negative ion,

$$k_2 = \tfrac{1}{2}(b^2-a^2)\log\frac{b}{a} \cdot \frac{1}{VT_2},$$

T_2 being the time between the two discontinuities P and Q.

In this experiment the inside diameter of the outer cylinder is 4·1 cm., and the outside diameter of the inner cylinder is 1·1 cm.

$\tfrac{1}{2}(b^2-a^2)\log b/a$ is therefore equal to $\tfrac{1}{8}(4{\cdot}1^2-1{\cdot}1^2)\log_e\left(\frac{4{\cdot}1}{1{\cdot}1}\right) = 2{\cdot}56$.

Therefore

$$k_1 = \frac{2{\cdot}56}{VT_1}, \qquad k_2 = \frac{2{\cdot}56}{VT_2}.$$

Several different forms of ionisation vessel were tried before one was

found which worked satisfactorily when immersed in liquid air. In several forms the strain on the ebonite insulation which was caused by the unequal contraction of ebonite and brass was sufficient to break the dielectric, while in another form this unequal contraction made the vessel leak and so liquid air made its entrance.

The form of vessel shown in longitudinal section in fig. 6, however, worked quite satisfactorily. V is a cylindrical brass vessel which contains the two brass electrodes A and B.

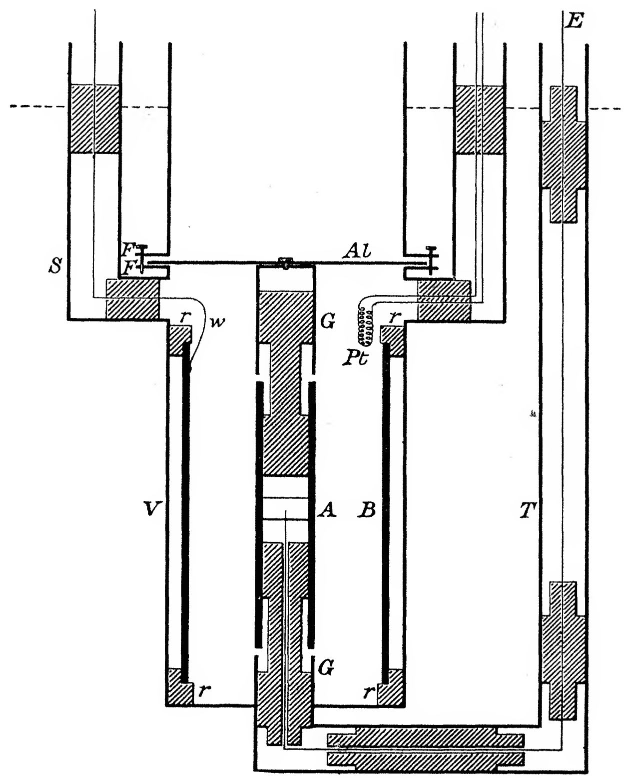


Fig. 6.

B is very little smaller than the vessel and is kept in position and insulated from it by means of ebonite rings at the top and bottom which are shown in section at *r*, *r*.

It is connected with the point *b* (fig. 5) by means of the wire *w* which is led out through ebonite plugs in the side tube S.

Through the centre of bottom of the vessel is soldered the lower guard tube G, while the upper guard tube is screwed to the centre of the aluminium lid Al.

The electrode A is supported between these two guard rings by means of ebonite plugs which are shown in section shaded, and it is connected to one of the mercury cups M (fig. 5) by means of a wire led out through the tube T.

The ebonite plugs are turned as shown in order to increase the insulating surface and so improve the insulation.

Pt is a platinum resistance which takes up very little space and which serves to measure the temperature of the air between the electrodes. The leads to this are led out through ebonite plugs in another side tube.

The aluminium lid Al fits into a depression which is turned in the lower flange F and is squeezed by screws between the two flanges F, F. The ebonite plugs are very close fitting so that the vessel is very nearly air-tight and a P_2O_5 drying tube, which is not shown, communicates with the interior of the vessel by means of another side tube.

The whole vessel and side tubes can be contained in a beaker 8 cm. diameter so that it may easily be immersed in liquid air up to the position indicated by the dotted line.

The Röntgen bulb is vertically above the vessel so that rays enter through the aluminium lid Al.

The standard vessel is of much simpler design, being merely a brass vessel with an aluminium window through which rays enter between two plane electrodes, one of which is connected to one end of the 160-volt battery, while the other is connected to one of the mercury cups M in fig. 5. A single reading is taken as follows :—

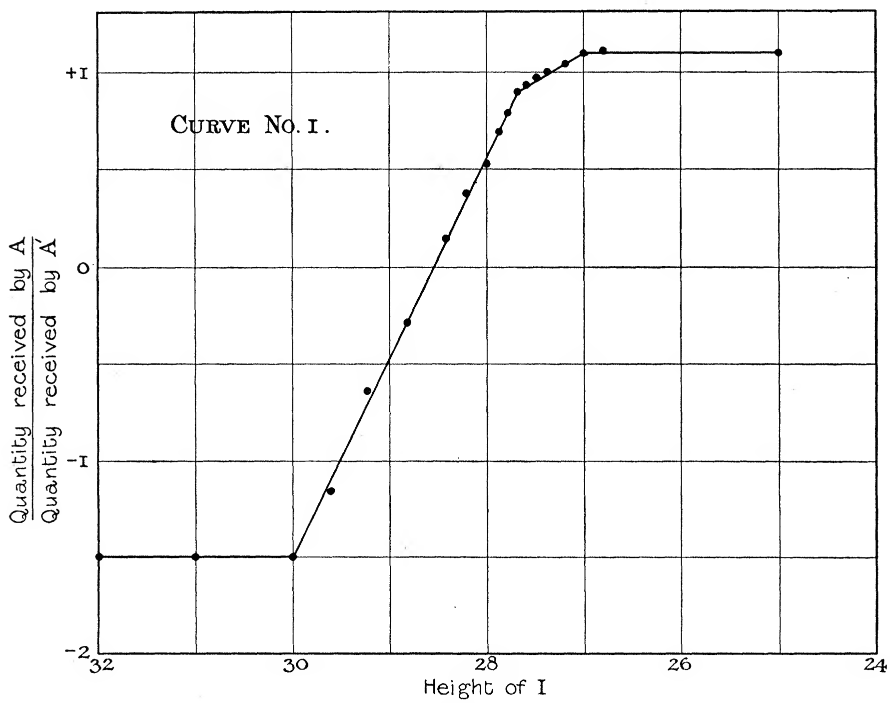
First I is placed at the required height on the scale and the contact is made. A, A′ and the electrometer are all earthed. The electro-magnet circuit is closed and the weights W and W′ are placed in position. A and A′ are insulated. The contact I′ is made and then the electro-magnet circuit is broken, allowing the weights to fall and break the contacts I and I′. The contact I is re-made and the quantities received by A and A′ are measured successively on the electrometer. The ratio of these two quantities is plotted against the scale reading of I.

A typical series at 12° C. is given on p. 173.

Plotting these quantities against each other we obtain Curve No. 1, from which we see that the points P, Q, and R occur at the scale readings 30 cm., 27·7 cm., and 27·0 cm., respectively.

Potential of cells = 80 volts.

Scale reading of I.	$\frac{\text{Quantity received by A}}{\text{Quantity received by A}'}$	Scale reading of I.	$\frac{\text{Quantity received by A}}{\text{Quantity received by A}'}$
32·0	−1·5	27·8	+0·80
31·0	−1·5	27·7	+0·90
30·0	−1·5	27·6	+0·94
29·6	−1·15	27·5	+0·98
29·2	−0·73	27·4	+1·00
28·8	−0·28	27·2	+1·04
28·4	+0·15	27·0	+1·10
28·2	+0·37	26·8	+1·10
28·0	+0·55	25·0	+1·10
27·9	+0·70		



When the contact breaker I is placed at 30 cm. on the scale the distance between it and the electro-magnet is 11·5 cm. The height of the falling weight itself is 4·2 cm., therefore the actual height of fall of the weight before breaking the contact = 7·3 cm.

Height of fall to 27·7 cm. = 9·6 cm.

„ „ 27·0 „ = 10·3 „

The time of fall to 30·0 cm. = $\sqrt{\frac{2 \times 7\cdot 3}{981}}$ sec. = 0·1220 sec.

$$\text{The time of fall to } 27{\cdot}7 \text{ cm.} = \sqrt{\frac{2\times 9{\cdot}6}{981}} \text{ sec.} = 0{\cdot}1400 \text{ sec.}$$

$$\text{,, } \quad 27{\cdot}0 \text{ ,, } = \sqrt{\frac{2\times 10{\cdot}3}{981}} \text{ sec.} = 0{\cdot}1450 \text{ sec.}$$

Therefore The time from P to Q = 0·0180 sec.

and ,, ,, P to R = 0·0230 ,,

$$k_1 = \frac{2{\cdot}56}{0{\cdot}023\times 80} = 1{\cdot}39 \text{ cm./sec. per volt/cm.}$$

$$k_2 = \frac{2{\cdot}56}{0{\cdot}018\times 80} = 1{\cdot}78 \quad\text{,,}\quad\quad \text{,,}$$

The results at ordinary temperatures show that the apparatus is working satisfactorily.

The following is a typical set of readings taken when the apparatus is immersed in liquid air up to the position indicated by the dotted lines in fig. 6.

Potential of cells = 82 volts. Resistance of Pt thermometer steady at 0·90 ohm.

Scale reading of I.	$\frac{\text{Quantity received by A}}{\text{Quantity received by A}'}$	Scale reading of I.	$\frac{\text{Quantity received by A}}{\text{Quantity received by A}'}$
32·0	−1·67	21·0	+0·162
30·0	−1·67	17·0	+0·60
29·3	−1·36	13·0	+1·01
28·34	−1·09	9·0	+1·36
27·82	−0·933	5·0	+1·60
26·8	−0·72	1·0	+1·60
25·0	−0·39	−5·0	+1·60
23·0	−0·10		

These numbers are plotted in Curve No. 2, which only shows two points of discontinuous curvature, the one occurring at the scale-reading 30 cm., the other at 5·5 cm.

This would lead us to the conclusion that the velocities of the positive and negative ions are equal to one another.

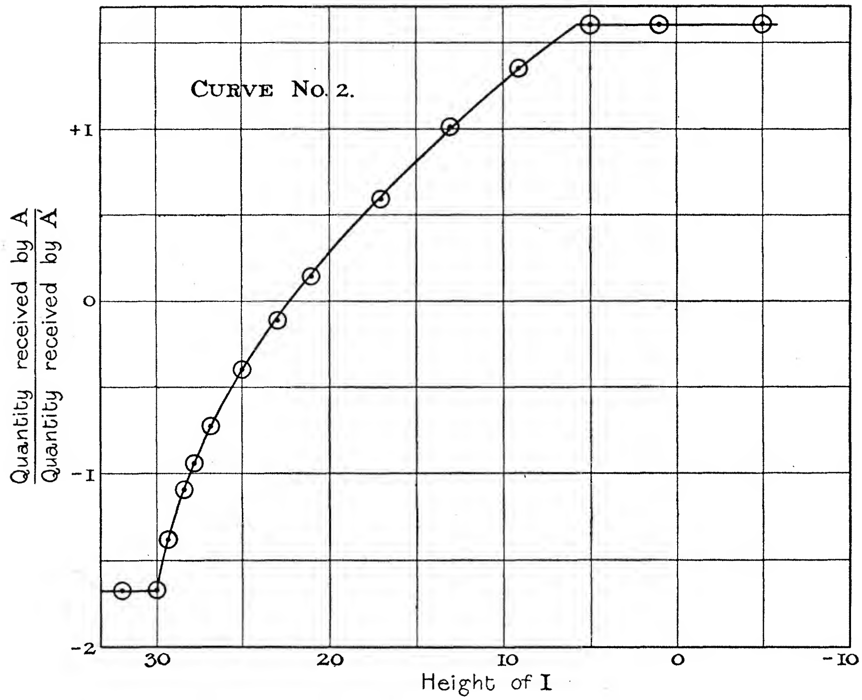
Time to fall to 30 cm. = 0·1220 sec.

$$\text{,, } \quad \text{,, } \quad 5{\cdot}5 \text{ ,, } = \frac{2\times 31{\cdot}8}{981} = 0{\cdot}2546 \text{ sec.}$$

Thus Time between discontinuities = 0·1346 sec.,

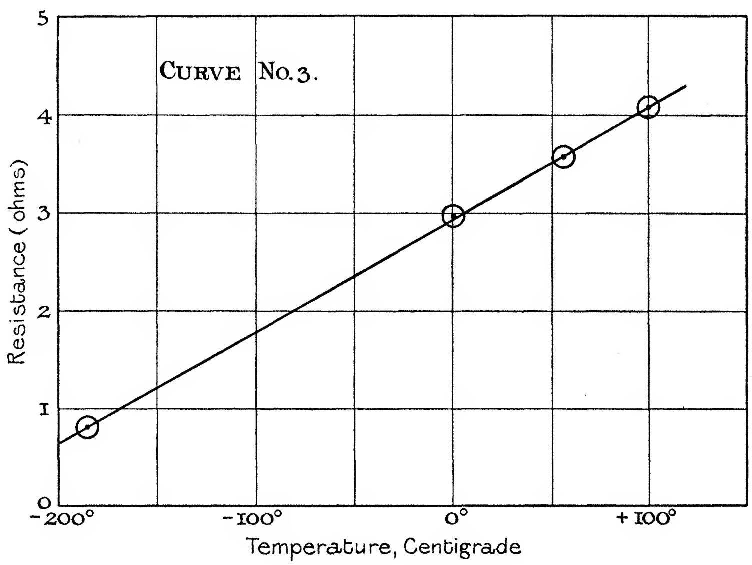
i.e., $$k_1 \text{ and } k_2 = \frac{2{\cdot}56}{82\times 0{\cdot}1346} = 0{\cdot}232 \text{ cm./sec. per volt/cm.}$$

To calibrate the platinum thermometer its resistance was found when



it was immersed in freshly prepared liquid air (—186° C.), water at 0° C., water at 57° C., and water at 100° C.

The calibration curve is given in Curve No. 3, which shows that when the resistance is 0·90 ohm the temperature is —180° C.



Temperature.	Resistance.
° C.	ohms.
−186	0·82
0	2·97
57	3·57
100	4·03

The disappearance of the one point of discontinuous curvature might be due to some defect in the apparatus; such a defect, for instance, as would arise from the difference of coefficient of expansion of ebonite and brass. This might conceivably allow the central electrode to get a little out of the centre, and this would very soon round off any corners in the curve. After taking several precautions to prevent such an occurrence, however, the other point does not reappear, and if we examine the curve the sharpness of the other discontinuities seems to show that there is no such defect.

Five series of readings were obtained with the vessel immersed in liquid air, and the curves obtained were exactly similar. The velocities found were :—

Velocity.	Temperature.
cm./sec. volt/cm.	° C.
0·232	−180
0·237	−179
0·239	−177
0·234	−180
0·235	−179
Mean 0·235	−179

i.e., at −179° C. the velocities of the positive and negative ions are each equal to 0·235 cm./sec. per volt/cm.

Determination of the Velocities at −65° C.—In this experiment the ionisation vessel consists of a double-walled metal jacket, inside which the electrodes are contained, and the space between the walls of which is filled with solid CO_2.

A diagram of the vessel is given in fig. 7.

In order to keep the space between the double walls filled with solid CO_2, liquid CO_2 is allowed to escape from a cylinder through a small hole. It enters the jacket through the tube E, which is screwed into the cylinder, and the gas is led out through the tubes L and allowed to escape outside the window.

Unfortunately a steady stream of CO_2 cannot be maintained in this way, for the small hole gets choked with the solid and so one cannot merely leave the stream flowing, but by keeping an eye on the temperature and blowing more CO_2 through when it shows signs of falling, it is quite easily maintained between the limits $-62°$ and $-68°$ C. The vessel was surrounded with three layers of thick felt in order to protect it from being warmed up too rapidly by external radiation.

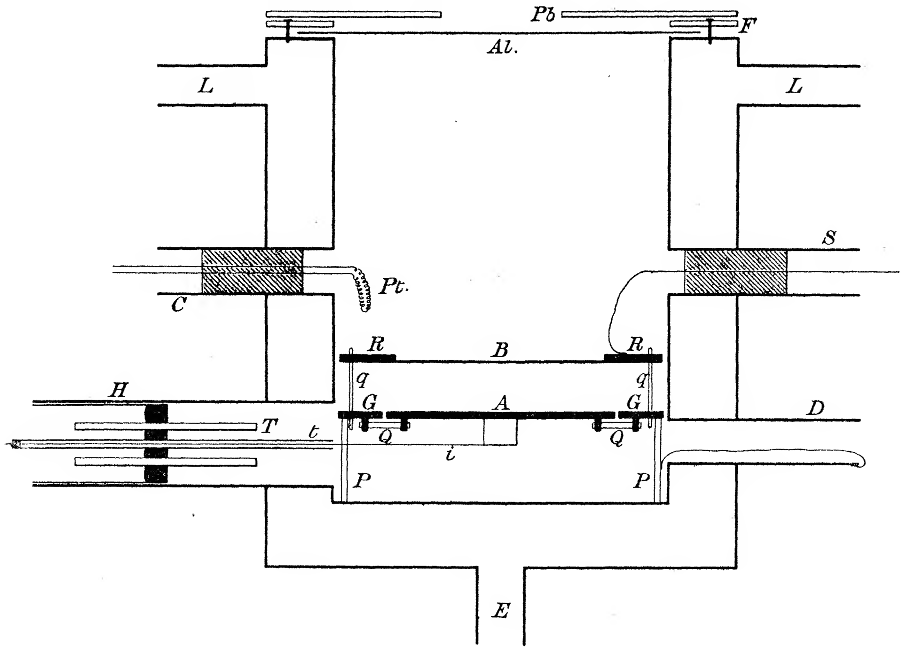


FIG. 7.

The electrode A is of thick brass, and is insulated from the guard ring G by means of three rods of quartz Q, whose ends are soldered to G and A respectively. The guard ring is supported by three brass pillars P, which are soldered to it and which rest on the base of the vessel.

The electrode B is of aluminium and is screwed to the brass ring R. It is supported by three quartz rods q, which are soldered into holes in G and R. Three spacing blocks, 0·96 cm. thick, were placed between A and B while the quartz rods q were being soldered, and thus the electrodes were fixed accurately parallel. The wire connecting B with the point b in fig. 5 is led out through an ebonite plug in the side tube S.

The wire i connecting A to a mercury cup (M in fig. 5) is threaded through a narrow brass tube t. This is soldered into the quartz tube T, which in its turn is soldered into a wider brass tube. This brass tube

slides tightly into the side tube H, making a fairly air-tight joint. The wire *i* is pulled taut, and is then soldered to the outer end of *t*.

The leads to the platinum thermometer Pt are led in through an ebonite plug in the side tube C.

The side tube D serves a double purpose. A P_2O_5 drying tube is attached to it, and through it a wire which is soldered to the guard ring is led out and soldered into good contact with the vessel.

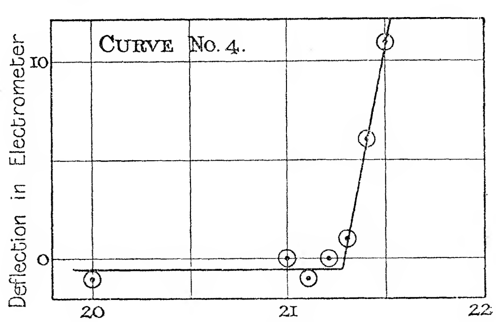
The lid of the vessel Al is of thin aluminium and is made fairly air-tight by being squeezed between a brass ring F and the top of the double-walled jacket. A lead shield Pb only allows the rays to impinge centrally on the electrodes.

Since the rays impinge directly on the brass electrode A, the secondary radiation makes the ionisation very intense close to A, so that in this case the null method is applied. The method of taking a reading is exactly the same as described for the temperature, $-179°$ C., except that the two electrodes A and A′ are connected together all the time instead of being connected separately to the electrometer. A typical series of readings is given below :—

Potential of cells = 85 volts. Electrode B is negative before reversal.

Scale reading of I.	Deflection in electrometer.
cm.	mm.
20·0	− 1
21·0	0
21·1	− 1
21·2	0
21·3	+ 1
21·4	+ 6
21·5	+11

These numbers are plotted in Curve No. 4 which shows that the point of discontinuity R is at 21·28 cm.



The resistance of the platinum thermometer never varied beyond the limits 2·31 and 2·25 ohms. Exactly similar series of readings were conducted to find the points P and Q.

The point P is at 25·25 cm. scale reading, and
" Q " 22·22 " "

Now the height of fall to 25·25 cm. = 59·70 cm.
" " 21·28 " = 63·67 "
" " 22·22 " = 62·73 "

Thus

$$\text{Time of fall to } 25{\cdot}25 = \sqrt{\frac{119{\cdot}4}{981}} = 0{\cdot}3490 \text{ sec.}$$

$$\text{" " } 21{\cdot}28 = \sqrt{\frac{127{\cdot}34}{981}} = 0{\cdot}3606 \text{ sec.}$$

$$\text{" " } 22{\cdot}22 = \sqrt{\frac{125{\cdot}46}{981}} = 0{\cdot}3580 \text{ sec.}$$

Thus

Time between P and Q = 0·0090 sec.,

and " P and R = 0·0116 "

Now distance between electrodes = 0·96 cm., and potential on electrodes = 0·85 volt. Thus

$$k_1 = \frac{0{\cdot}96}{0{\cdot}0116} \times \frac{0{\cdot}96}{85} = 0{\cdot}935 \text{ cm./sec. per volt/cm.}$$

$$k_2 = \frac{0{\cdot}96}{0{\cdot}0090} \times \frac{0{\cdot}96}{85} = 1{\cdot}21 \text{ " "}$$

Inspecting the Pt thermometer calibration curve, we see that the temperature is between $-62°$ and $-68°$ C. The mean temperature is thus $-65°$ C.

Owing to the large amount of CO_2 which was required to keep the temperature constant, only three series of readings could be taken before the cylinder of liquid CO_2 was exhausted. The results of these three series are:—

	k_1.	k_2.	Temperature Limits.	Mean Temperature.
			°C.	°C.
	0·935	1·21	−62 to −68	−65·0
	0·95	1·25	−60 to −65	−62·5
	0·95	1·22	−61 to −66	−63·5
Mean	0·945	1·23	—	−63·7

Determinations of the velocities at temperatures 12° *C. to* 138° *C.*—These determinations have been made with two different forms of ionisation vessel. The first form of ionisation vessel is the same as that used for $-65°$.

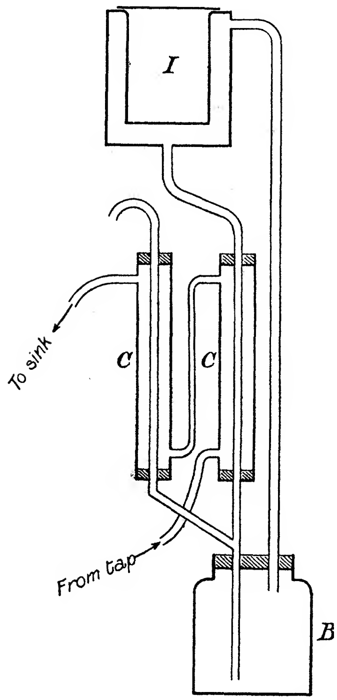


Fig. 8.

A boiler and two condensers were fitted up as in fig. 8 so that a rapid stream of vapour could be driven through the jacket in fig. 7 and condensed back again into the boiler. B is the boiler, C, C are two condensers and I is the double-walled ionisation vessel. Three different liquids were used in B, methylated spirits, water and amyl alcohol, giving temperatures of 75°, 100° and 126° respectively.

Exactly the same operations were gone through in this case as were gone through in the determinations at $-65°$ C. A null method was used and the points P, Q, and R found by travelling along the horizontal parts of the curves until a deflection was obtained.

A number of determinations were made at the ordinary temperature of the room and the following values of k_1 and k_2 were obtained :—

k_1.	k_2.	Temperature.
		°C.
1·38	1·77	12
1·39	1·77	11
1·41	1·80	12
1·37	1·78	11
1·41	1·81	14
Mean 1·39	1·79	12

Probably the most accurate determinations so far are those of Langevin and Zeleny. Their results are :—

	k_1.	k_2.
Langevin.........	1·40	1·70
Zeleny............	1·36	1·87

We may, therefore, conclude that the apparatus is working quite satisfactorily.

The series of experiments with the jacket heated to 75° C. by means of methylated spirits gave the following results:—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
	cm.	cm.	sec.	sec.	volts.	
1	25 ·25	59 ·70	0 ·3490			
	22 ·89	62 ·06	0 ·3557	0 ·0067	81	1 ·69
	23 ·38	61 ·57	0 ·3543	0 ·0053	—	2 ·14
2	25 ·25	59 ·70	0 ·3490			
	22 ·95	62 ·00	0 ·3555	0 ·0065	—	1 ·67
	23 ·43	61 ·52	0 ·3541	0 ·0051	85	2 ·12
3	25 ·25	59 ·70	0 ·3490			
	22 ·85	62 ·10	0 ·3558	0 ·0068	80	1 ·69
	23 ·33	61 ·62	0 ·3544	0 ·0054	—	2 ·13
4	25 ·25	59 ·70	0 ·3490			
	22 ·90	62 ·05	0 ·3557	0 ·0067	84	1 ·62
	23 ·40	61 ·55	0 ·3542	0 ·0052	—	2 ·11

From these experiments we have:—

	k_1.	k_2.	Temperature.
			° C.
	1 ·69	2 ·14	+75
	1 ·67	2 ·12	
	1 ·69	2 ·13	
	1 ·62	2 ·11	
Mean	1 ·67	2 ·125	+75

With the boiler filled with water, *i.e.*, with the vessel maintained at 100° C., the following results were obtained:—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
	cm.	cm.	sec.	sec.	volts.	
All expts. P at	25 ·25	59 ·70	0 ·3490			
1	22 ·99	61 ·96	0 ·3554	0 ·0064	80	1 ·80
	23 ·44	61 ·51	0 ·3541	0 ·0051	—	2 ·26
2	23 ·15	61 ·80	0 ·3550	0 ·0060	85	1 ·81
	23 ·52	61 ·43	0 ·3539	0 ·0049	—	2 ·21
3	23 ·15	61 ·80	0 ·3550	0 ·0060	83	1 ·85
	23 ·48	61 ·47	0 ·3540	0 ·0050	—	2 ·22
4	22 ·99	61 ·96	0 ·3554	0 ·0064	82	1 ·76
	23 ·41	61 ·54	0 ·3542	0 ·0052	—	2 ·16
5	23 ·15	61 ·80	0 ·3550	0 ·0060	84	1 ·83
	23 ·48	61 ·47	0 ·3540	0 ·0050	—	2 ·19

Thus we have at 100° C.:—

k_1.	k_2.
1 ·80	2 ·26
1 ·81	2 ·21
1 ·85	2 ·22
1 ·76	2 ·16
1 ·83	2 ·19
Mean 1 ·81	2 ·21 cm./sec. per volt/cm.

With the boiler filled with amyl alcohol, *i.e.*, with the vessel at a temperature of 126° C., the following results were obtained :—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	*k*.
All expts. P at	cm. 25 ·25	cm. 59 ·70	sec. 0 ·3490	sec.	volts.	
1	23 ·34 23 ·69	61 ·61 61 ·26	0 ·3544 0 ·3534	0 ·0054 0 ·0044	89 —	1 ·91 2 ·36
2	23 ·24 23 ·62	61 ·71 61 ·33	0 ·3547 0 ·3536	0 ·0057 0 ·0046	82 —	1 ·97 2 ·44
3	23 ·31 23 ·66	61 ·64 61 ·29	0 ·3545 0 ·3535	0 ·0055 0 ·0045	85 —	1 ·97 2 ·41
4	23 ·15 23 ·52	61 ·80 61 ·43	0 ·3550 0 ·3539	0 ·0060 0 ·0049	80 —	1 ·92 2 ·36
5	23 ·31 23 ·66	61 ·64 61 ·29	0 ·3545 0 ·3535	0 ·0055 0 ·0045	84 —	1 ·99 2 ·43

Thus we have at +126° C. :—

k_1.	k_2.
1 ·91	2 ·36
1 ·97	2 ·44
1 ·97	2 ·41
1 ·92	2 ·36
1 ·99	2 ·43
Mean 1 ·95	2 ·40 cm./sec. per volt/cm.

The velocities of the ions at 13°, 60°, 110° and 138° were also found by means of another ionisation vessel. It is shown in section in fig. 9.

The vessel itself, V, is a brass casting of which the inside dimensions are about 4 × 4 × 2 inches. A and B are two brass electrodes and G is a guard ring. A and B are fixed in position by being screwed to brass rods which are soldered into quartz tubes Q, Q, while these in their turn are soldered into the cups C, C, which are turned in the sides of the vessel. While the solder is being poured into the cups the two electrodes are fixed parallel and 0·96 cm. apart by means of three spacing blocks.

The two tubes S and T fit on to the outside of the cups, and are soldered in position. Through them the connections to B and A are made by means

of the two brass rods E, H, which screw into little blocks on the ends of *r*, *r*.

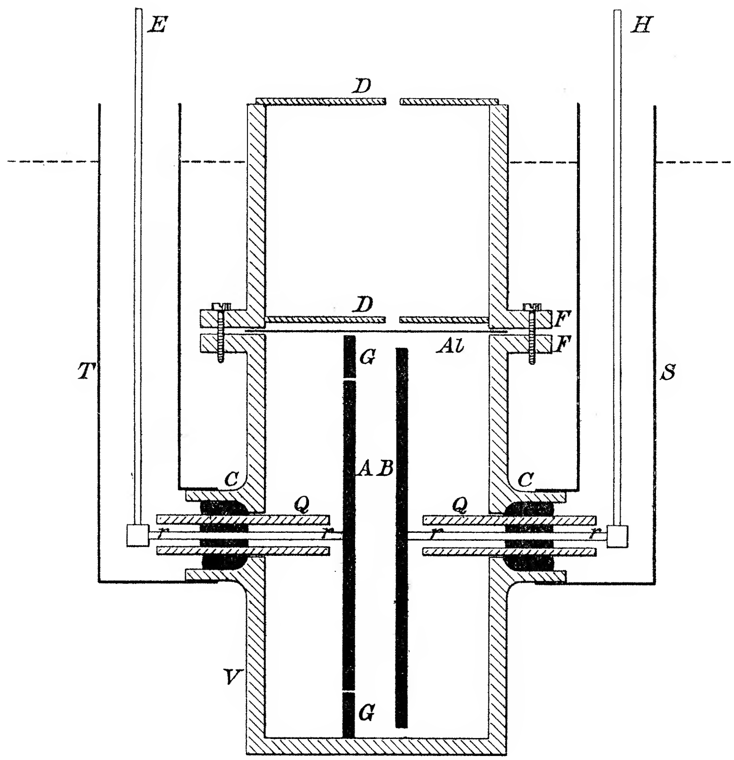


Fig. 9.

Al is the aluminium lid to the vessel and is made tight by being squeezed between the two flanges F, F.

D, D are two brass diaphragms which only allow a flat pencil of rays about 3 mm. thick to enter the vessel, and which are so placed that this pencil just grazes the surface of B. There is a continuation of the vessel above the aluminium lid so that the whole may be immersed in an oil bath up to about the position indicated by the dotted lines.

The oil bath can be maintained at any constant temperature between about 30° and 150° by means of a thermostat.

The mode of using this vessel was exactly the same as in the last experiments. A null method was used and the height of the movable contact breaker I varied, to find the point at which one begins to get a permanent deflection. With this apparatus the point was very sharply marked.

The following results were obtained when the vessel was at the temperature of the laboratory :—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
All expts. P at	cm. 29 ·35	cm. 56 ·72	sec. 0 ·3400	sec.	volts.	
1. 12° C.	26 ·69 27 ·27	59 ·38 58 ·80	0 ·3479 0 ·3462	0 ·0079 0 ·0062	84 —	1 ·39 1 ·77
2. 13° C.	26 ·83 27 ·37	59 ·24 58 ·70	0 ·3475 0 ·3459	0 ·0075 0 ·0059	88 —	1 ·40 1 ·77
3. 11° C.	26 ·52 27 ·16	59 ·55 58 ·91	0 ·3484 0 ·3466	0 ·0084 0 ·0066	80 —	1 ·37 1 ·75
4. 15° C.	26 ·71 27 ·30	59 ·36 58 ·77	0 ·3478 0 ·3461	0 ·0078 0 ·0061	83 —	1 ·42 1 ·82

Thus we have :—

k_1.	k_2.	Temperature.
		° C.
1 ·39	1 ·77	12
1 ·40	1 ·77	13
1 ·37	1 ·75	11
1 ·42	1 ·82	15
Mean 1 ·395	1 ·78	13

The following results were obtained with the oil bath maintained at 60° C. :—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
All expts. P at	cm. 29 ·35	cm. 56 ·72	sec. 0 ·3400	sec.	volts.	
1	27 ·07 27 ·51	59 ·00 58 ·56	0 ·3468 0 ·3455	0 ·0068 0 ·0055	84 —	1 ·61 1 ·99
2	27 ·05 27 ·53	59 ·02 58 ·54	0 ·3469 0 ·3454	0 ·0069 0 ·0054	84 —	1 ·59 2 ·03
3	27 ·15 27 ·59	58 ·92 58 ·48	0 ·3466 0 ·3453	0 ·0066 0 ·0053	86 —	1 ·62 2 ·02
4	26 ·92 27 ·39	59 ·15 58 ·68	0 ·3473 0 ·3459	0 ·0073 0 ·0059	80 —	1 ·58 1 ·95

Thus we have at 60° C. :—

	k_1.	k_2.
	1 ·61	1 ·99
	1 ·59	2 ·03
	1 ·62	2 ·02
	1 ·58	1 ·95
Mean	1 ·60	2 ·00 cm./sec. per volt/cm.

With the oil bath maintained at 110° C. the following results were obtained :—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
	cm.	cm.	sec.	sec.	volts.	
All expts. P at	29 ·35	56 ·72	0 ·3400			
1	27 ·37	58 ·70	0 ·3459	0 ·0059	84	1 ·86
	27 ·77	58 ·32	0 ·3448	0 ·0048	—	2 ·28
2	27 ·23	58 ·84	0 ·3464	0 ·0064	80	1 ·80
	27 ·67	58 ·40	0 ·3450	0 ·0050	—	2 ·30
3	27 ·29	58 ·78	0 ·3462	0 ·0062	80	1 ·85
	27 ·70	58 ·37	0 ·3449	0 ·0049	—	2 ·35
4	27 ·40	58 ·67	0 ·3459	0 ·0059	83	1 ·88
	27 ·70	58 ·37	0 ·3449	0 ·0049	—	2 ·26

Thus we have :—

	k_1.	k_2.
	1 ·86	2 ·28
	1 ·80	2 ·30
	1 ·85	2 ·35
	1 ·88	2 ·26
Mean	1 ·85	2 ·30 cm./sec. per volt/cm. at 110° C.

With the oil bath maintained at 138° C. the following results were obtained:—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	*k*.
All expts. P at	cm. 29·35	cm. 56·72	sec. 0·3400	sec.	volts.	
1	27·53	58·54	0·3454	0·0054	85	2·00
	27·89	58·18	0·3443	0·0043	—	2·52
2	27·49	58·58	0·3456	0·0056	84	1·96
	27·86	58·21	0·3445	0·0045	—	2·44
3	27·53	58·54	0·3455	0·0055	84	1·99
	27·89	58·18	0·3444	0·0044	—	2·49
4	27·58	58·49	0·3453	0·0053	85	2·05
	27·92	58·15	0·3443	0·0043	—	2·53

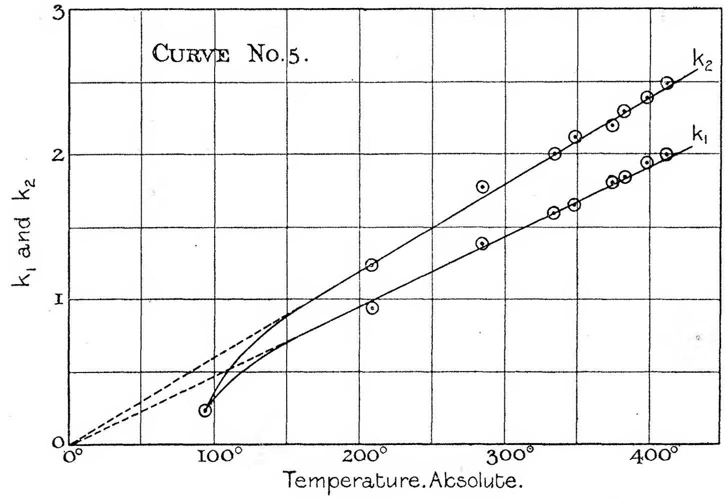
Thus we have:—

k_1.	k_2.
2·00	2·52
1·96	2·44
1·99	2·49
2·05	2·53
Mean 2·00	2·495 cm./sec. per volt/cm. at 138° C.

Collecting all the results at the different temperatures we get:—

k_1.	k_2.	Temperature absolute.
		° C.
2·00	2·495	411
1·95	2·40	399
1·85	2·30	383
1·81	2·21	373
1·67	2·125	348
1·60	2·00	333
1·39	1·785	285
0·945	1·23	209
0·235	0·235	94

These numbers are plotted in Curve No. 5.



We see that except for the case of the velocities at 94° abs. the points lie very close to straight lines through the origin, *i.e.*, k_1 and k_2 are very nearly proportional to the absolute temperature. This is a strangely simple result when we consider what a complication of circumstances affects the velocities.

Interpretation of the Results.—As is well known, by making use of the kinetic theory of gases, we can obtain an expression for the drift velocity U of an ion in an electric field in the form

$$U = \tfrac{1}{2}\frac{e}{m_2}\frac{\lambda_2}{v_2}X,$$

where X is the field,

m_2 is the mass of the ion,

λ_2 is the mean free path of the ion, and

v_2 is the mean molecular velocity of the ion.

This formula depends upon the fundamental assumptions—

1. That statically the previous history of the ion is wiped out at each collision.
2. That the drift velocity is small compared with the mean molecular velocity. This condition is easily fulfilled.

It is easy to see that the first assumption is correct if the ions consist of one molecule each, but it is probably not quite accurate when they consist of more than one. It is difficult, however, to make any other workable assumption and, if we make it, it is fairly simple to find U in terms of m_1, λ_1, v_1 (the corresponding quantities for the gas molecules), and n, the number of molecules which go to make up one ion.

For let N_1 be the number of molecules per cubic centimetre, and

N_2 „ „ ions „ „

Let r_1 be the radius of a molecule, and r_2 of an ion $= n^{\frac{1}{3}}r$,

$2r_{12} =$ distance between centres of a molecule and an ion at a collision $= (r_1+r_2)$,

$v_2 = v_1/\sqrt{r}$.

Then, treating the mixture of ions and molecules as a mixture of two different gases, the mean free path, λ_2, of an ion is given by

$$\lambda_2^{-1} = \pi\left[\mathrm{N}_2 r_2^2\left(1+\frac{m_2}{m_2}\right)^{\frac{1}{2}} + \mathrm{N}_1 r_{12}^2\left(1+\frac{m_2}{m_1}\right)^{\frac{1}{2}}\right].*$$

Now N_2 is negligible compared with N_1; thus

$$\lambda_2^{-1} = \Pi \mathrm{N}_1 r_{12}^2 (1+n)^{\frac{1}{2}} = \tfrac{1}{4}\Pi \mathrm{N}_1 r_1^2 (1+n^{\frac{1}{3}})^2 (1+n)^{\frac{1}{2}}$$
$$= \tfrac{1}{8}\sqrt{2}\,\lambda_1 (1+n^{\frac{1}{3}})^2 (1+n)^{\frac{1}{2}}.$$

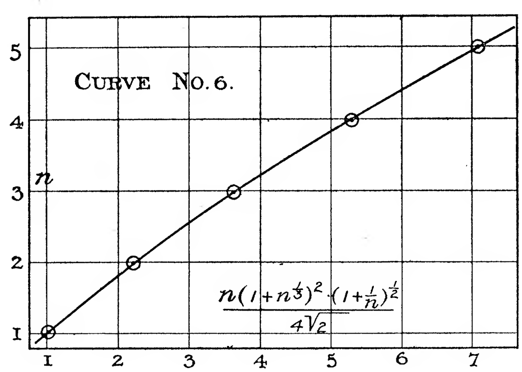
Thus

$$\frac{e}{m_2}\,\frac{\lambda_2}{v_2} = \left[\frac{4\sqrt{2}}{n\,(1+n^{\frac{1}{3}})^2\left(1+\dfrac{1}{n}\right)^{\frac{1}{2}}}\right]\frac{e}{m_1}\,\frac{\lambda_1}{v_1}.$$

The factor in the brackets is too complex for one to see at a glance how it varies with n. The following are the values of its inverse when $n = 1, 2, 3, 4$, and 5:—

$n = 1$	1
2	2·21
3	3·65
4	5·31
5	7·12

These are plotted in Curve No. 6.



Now the value of $\frac{1}{2}\,\frac{e}{m_1}\,\frac{\lambda_1}{v_1}$ for air at 76 cm. pressure and 0° C. is equal to 770, when we use the values for the size of the molecules given in Jeans'

* Jeans, 'Dyn. Theory of Gases,' p. 234.

'Dyn. Theory of Gases,' p. 340, the number of molecules per cubic centimetre given by the electrical methods of J. J. Thomson and H. A. Wilson, and the electrolytic values of e/m. These, I think, are the most reliable values we can get.

The velocity of the positive ion given by Curve 5 is about 1·33 cm./sec. per volt/cm., *i.e.*, 399 cm./sec. per absolute unit of field, at 0° C.

This is 1·93 times too small, therefore

$$\frac{n(1+n^{\frac{1}{3}})^2\left(1+\frac{1}{n}\right)^{\frac{1}{2}}}{4\sqrt{2}} = 1{\cdot}93.$$

From Curve 6 we see that this would require n to be about 1·8. That is at 0° C. and 76 cm. pressure a positive ion in air consists on an average of 1·8 molecules.

M. Langevin* found it necessary, in order to explain the slowness of diffusion of the ions, to assign to them a size twice or thrice the size of a molecule, while Dr. Richardson,† from considerations based on the variation of the ionic velocities with pressure, came to the conclusion that a positive ion in air at atmospheric pressure and at ordinary temperatures consists of about 3 molecules.

By making the same calculation as the above from the experimental results at different temperatures, we get the variation with temperature of the number of molecules in the ion. The calculated values of n are given in the following table:—

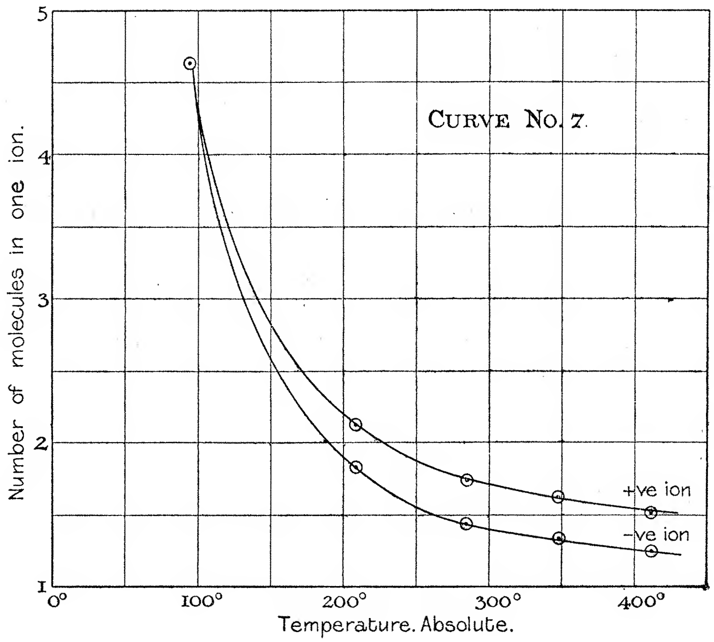
Temperature absolute.	n (positive).	n (negative).
° C.		
94	4·63	4·63
209	2·12	1·82
285	1·76	1·43
348	1·64	1·34
411	1·52	1·25

These numbers are plotted in Curve No. 7.

Of course, the first assumption made in deducing the formula $\frac{1}{2} \times \frac{e}{m}\frac{\lambda}{v}$ will show us that we cannot accurately deduce the number of molecules in an ion in this way. Probably all the numbers have to be multiplied by a factor which is not very far different from unity, but at least this curve will show us how the size of the ion varies with the temperature.

* 'Comptes Rendus,' vol. 111, p. 35, 1905.

† 'Phil. Mag.,' July, 1905.



The fact that it varies continuously and not in jumps would seem to show that there is a continual exchange going on between ions and uncharged molecules; at some collisions several molecules remain attached to the ion, while at others one or more of them is knocked off, and so a dynamical equilibrium is set up.

As the temperature of the gas rises, the collisions are more violent, and statistically fewer molecules are attached to an ion; this gradual change would go on until the collisions become so violent that at times corpuscles are shot off without even a single molecule attached to them. When this happens the velocity of the ion would very rapidly increase with the temperature, and so in flames we might expect those rapidly moving ions which are unloaded corpuscles for an appreciable fraction of their life.

In conclusion, I wish to express my indebtedness to Professor J. J. Thomson for suggesting this subject for investigation and for the kindly interest he has shown while the experiments have been in progress. I also wish to thank Dr. Richardson for some helpful suggestions.